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(54) A METHOD AND APPARATUS FOR BREAKING DOWN DEPOSITS ON THE WALLS OF A VESSEL CONTAINING A POTENTIALLY EXPLOSIVE GAS MIXTURE

(71) We, BOC LIMITED, of Hammersmith House, London, W6 9DX, England, an English company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process and apparatus for cleaning vessels containing a potentially explosive gas mixture.

Many instances arise in which a storage vessel can acquire a potentially dangerous content of gas. One of the most commonly encountered is that of storage tanks for substances such as liquid petroleum products. These tanks tend to acquire a dangerous mixture of air and gaseous hydrocarbons upon removal of the liquid products and deposits in the form of a scum tend to build-up on the tank walls. Additional problems, notably the build-up of static electricity, arise if the tank is on board a sea-going vessel. The invention is concerned with providing a method of cleaning such tanks which minimizes the risk of explosion.

According to the invention, there is provided a method of breaking down deposits on the walls of a vessel containing a potentially explosive gas mixture which method comprises introducing into the vessel liquid which is non-combustible and does not support combustion, (for example, sea water for vessels on sea-going craft), the liquid containing or being provided with micro-organisms of a type suitable to break-down the deposits, and the liquid containing or being provided with an oxygen-containing gas so as to enhance the activity of the micro-organisms; and supplying an inert gas to the ullage space in the vessel at a rate to reduce the oxygen content of the gas mixture in the ullage space to below that which will support combustion. Typically, the oxygen content of the gas mixture in the ullage space is reduced to below 5% by volume. The invention also provides apparatus for breaking down deposits on the walls of a vessel containing a potentially explosive gas mixture which apparatus comprises means for introducing into the vessel a liquid which is non-combustible and does not support combustion, a source of oxygen-containing gas and means for introducing such gas into the liquid, in use, contained in the vessel so as to enhance the activity of micro-organisms existing, in use, in such liquid, and a source of inert gas and means to supply such inert gas to an ullage space defined, in use, between the surface of liquid in the vessel and the walls of the vessel.

The preferred liquid is sea water in which the oxygen-containing gas will dissolve at least to some extent. Preferably the oxygen-containing gas has a oxygen content higher than that of air, and preferably an oxygen content of at least 60% by volume. Most preferably the oxygen content of such gas will be at least 80%, and desirably not less than 90% by volume. The higher the oxygen content the more easily will the gas dissolve in water, when used as the aforesaid liquid.

Preferably the aforesaid inert gas is a nitrogen-rich gas, containing at least 90%, and preferably at least 95%, by volume nitrogen.

A convenient plant for providing both oxygen-rich gas and nitrogen-rich gas for use in a process according to the invention would be a pressure swing absorption unit using an absorbent which preferentially adsorbs either oxygen or nitrogen from air passed through the adsorbent. Preferably a multi-bed adsorbent unit is used so that substantially continuous flows of oxygen-rich and nitrogen-rich gas are obtained from the unit.

However, for many applications oxygen and nitrogen rich gases may be supplied and stored in liquefied form, e.g. in vacuum insulated evaporators (V.I.E) or in cylinders in gaseous form under pressure. The V.I.E's or cylinders would be located for example on site at a land based oil installation and

pressurised gas would be delivered therefrom as and when any oil tank required cleaning by a process according to the invention.

When the aforesaid liquid is water, the oxygen-rich gas is preferably introduced into the water, which fills the vessel, in fine bubble form so that a substantial proportion of the gas dissolves in the water before reaching the surface thereof. A typical concentration of the oxygen in the water would be in the range 3 to 8 parts per million, for example 4 ppm.

Many different methods of introducing the oxygen-rich gas into the water can be adopted according to which dissolving of the gas in the water is expedited. For example, if the vessel is sufficiently deep the gas may be introduced at the bottom of the vessel through a diffuser in fine bubble form so that the gas dissolves before reaching the surface of the liquid. The gas may be introduced into a stream of liquid, usually water, which is then passed into the main body of liquid in the vessel. Such stream may be withdrawn from the main body of liquid. The gas may be introduced into a pressurised stream of water so that the stream contains discrete oxygen-rich gas bubbles of undissolved gas. This stream may then be introduced into the water in the vessel under turbulent conditions so that the bubbles of undissolved gas are broken into extremely fine bubbles which dissolve in, or are consumed within, the body of the water before reaching the surface thereof.

Alternatively, it would be possible to pass the stream downwardly through a gas/liquid contactor device comprising a hollow chamber of sufficient cross-sectional area to reduce the velocity of the stream to prolong gas/liquid contact time, a stream of liquid and dissolved gas passing from the chamber to the liquid in the vessel. The chamber could be positioned in the liquid in the vessel or it could be positioned outside such vessel. The chamber may have lengths of increasing cross-sectional area in the downward direction to progressively reduce the velocity of the flow through the chamber. Only very fine bubbles carried in the stream should emerge from the lower end of the chamber and these bubbles will readily dissolve in the water outside the chamber before reaching the surface thereof.

The aforesaid stream of water which is pressurised is preferably withdrawn from the body of water in the vessel. Said stream may be introduced into the water in the vessel through a movable jet which can be operated to direct the stream across the walls of the vessel in order to help scour the sludge from the walls so that the micro-organisms can more readily break it down. A method similar to that described in our Co-pending Application Serial No. 1 504 510 can be adopted. A rotatable jet may be provided within the vessel through which said stream is directed at high velocity at the walls of the vessel, the jet being rotatable about a generally vertical axis. The jet may also be movable along such axis or may be mounted for tilting as well as rotary movement so as to be able to direct the jet of oxygenated liquid over substantially the entire inner surface of the vessel.

One embodiment of the invention will now be described by way of example and with reference to the accompanying drawings in which Figure 1 is a diagrammatic representation of an oil tank fitted with apparatus for breaking down deposits in the tank and embodying the invention; and, Figure 2 is a diagrammatic representation of a modified form of the sparging nozzle equipment of the apparatus of Figure 1.

Referring to the drawing, there is shown an oil tank 10 which may be one of a plurality of such tanks for crude oil which tanks are provided on an oil tanker. The tanker is provided with thirty or more of such tanks. In other embodiments, the tank may be part of a land installation, e.g. at a refinery.

In order to break down deposits or scum left on the walls of the tank after the oil has been removed, the tank is first filled with sea water through pipe 11, which is part of a standard sea water ballast supply system provided on oil tankers. An ullage space 9 will always exist above the surface of the water in which a potentially explosive gas mixture can collect. The water contains bacteria which break down the oil scum left on the walls of the tank. However, the bacteria need a supply of oxygen in order to remain active to break down such scum. A multi-bed pressure swing adsorption unit 12 is provided, each bed containing an adsorbent which preferentially adsorbs nitrogen, e.g. zeolite or oxygen e.g. activated carbon, from an air supply. In the example shown, nitrogen is adsorbed and an oxygen-rich gas is delivered from each bed during one phase of the pressure-swing cycle through line 14. During another phase of the cycle, a nitrogen-rich gas is desorbed from the adsorbent beds by a vacuum pump and withdrawn through line 16. The cycles of the adsorbent beds are timed to be out of phase with one another such that a substantially continuous flow of oxygen-rich gas is delivered through line 14 and a substantially continuous flow of nitrogen-rich gas is delivered through line 16.

The oxygen-rich gas in line 14 is introduced in fine bubble form into a pressurised stream of water in line 19, which is withdrawn from tank 10, in a venturi gas/water mixer 15. The pressurised stream containing dissolved and undissolved oxygen-rich gas is introduced into tank 10 though nozzles 17

provided in tubular arms 18 of a sparger assembly which arms are fed from a vertical conduit 20. The nozzles 17 deliver high velocity jets of water and can be arranged and designed to direct such jets so as to assist in scouring the sludge deposited on the walls of the tank. The bubbles of gas in the stream are shattered into micro-bubbles most of which dissolve in the water before reaching the surface of the water. The nitrogen-rich gas is introduced into the ullage space 9 in the tank 10 at a rate to maintain the oxygen content of the resultant gas mixture in the ullage space at below 5% by volume so that the risk of explosion is accordingly greatly reduced. The ullage space 9 is vented at a controlled rate through vent 21 to remove the carbon dioxide produced as a result of the break down of the oil deposits.

It will be appreciated that the above described pressure swing adsorption system for providing oxygen and nitrogen rich gases is convenient for some applications, particularly on board an oil tanker. However, in other applications the gases may be supplied in liquid or gaseous form from a bulk source of such gases, e.g. a cryogenic air separation plant. Many of the latter applications could be land based oil installations, e.g. oil refineries.

Referring to Figure 2, an alternative sparging device for the oxygenated water stream is shown which directs high velocity streams of water over the walls of the tank to assist in scouring sludge therefrom.

The central supply conduit 20 has rotatably mounted thereon an annular housing 21 in which a number of pivotally mounted jets 22 are carried. The housing 21 is rotated by a positive displacement pump 23 of the eccentric piston type which is carried at the lower end of conduit 20 and is driven by pressurised water taken from the interior of the conduit.

The jets are pivoted up and down as the housing 21 is rotated in order to direct high velocity streams of oxygenated water over the walls of the oil tank. The jets are connected through ball and socket joints 24 to pushrods 25, the lower ends of which rest on an inclined surface 26 of an annular cam 27 suspended from the lower end of the conduit 20.

WHAT WE CLAIM IS:—

1. A method of breaking down deposits on the walls of a vessel containing a potentially explosive gas mixture which method comprises introducing into the vessel liquid which is non-combustible and does not support combustion, the liquid containing or being provided with micro-organisms of a type suitable to break-down the deposits, and the liquid containing or being provided with an oxygen-containing gas so as to enhance the activity of the micro-organisms; and supplying an inert gas to the ullage space in the vessel at a rate to reduce the oxygen content of the gas mixture in the ullage space to below that which will support combustion.

2. A method as claimed in claim 1 wherein the oxygen content of the gas mixture in the ullage space is reduced to below 5% by volume.

3. A method as claimed in claim 1 or in claim 2 wherein the liquid is water.

4. A method as claimed in claim 3 wherein the liquid is sea water.

5. A method as claimed in any preceding claim wherein the oxygen-containing gas has an oxygen content higher than that of air.

6. A method as claimed in any preceding claim wherein the oxygen-containing gas has an oxygen content of at least 60% by volume.

7. A method as claimed in any preceding claim wherein the oxygen content of the oxygen-containing gas is at least 80% by volume.

8. A method as claimed in any preceding claim wherein the oxygen content of the oxygen-containing gas is at least 90% by volume.

9. A method as claimed in any preceding claim wherein the aforesaid inert gas is a nitrogen-rich gas.

10. A method as claimed in any preceding claim wherein the inert gas contains at least 90% nitrogen by volume.

11. A method as claimed in any preceding claim wherein the inert gas contains at least 95% nitrogen by volume.

12. A method as claimed in any preceding claim in which the inert gas is a nitrogen-rich gas wherein the oxygen-containing gas and the nitrogen-rich gas are separated from an air feedstock.

13. A method as claimed in claim 12 wherein the air feedstock is separated as aforesaid by contacting it with an adsorbent material, which preferentially adsorbs oxygen or nitrogen.

14. A method as claimed in any preceding claim in which the aforesaid liquid is water, wherein the oxygen-rich gas is introduced into the water, in fine bubble form so that a substantial proportion of the gas dissolves in the water before reaching the surface thereof.

15. A method as claimed in claim 14 wherein the gas is introduced at the bottom of the vessel through a diffuser in fine bubble form so that the gas dissolves before reaching the surface of the liquid.

16. A method as claimed in claim 14 wherein the gas is introduced into a stream of liquid which is then passed into the main body of water in the vessel.

17. A method as claimed in claim 15 wherein the stream is withdrawn from the main body of liquid in the vessel.

18. A method as claimed in claim 16 or 17 wherein the gas is introduced into a pres-

surised stream of water so that the stream containing discrete bubbles of undissolved gas, the stream being introduced into the water in the vessel under turbulent conditions so that the bubbles of undissolved gas are broken into extremely fine bubbles which dissolve in, or are consumed within, the body of the water before reaching the surface thereof.

19. A method as claimed in claim 16 or 17 wherein the gas is introduced into a stream of water which passes downwardly through a gas/liquid contactor device comprising a hollow chamber of sufficient cross-sectional area to reduce the velocity of the stream to provide prolonged gas/liquid contact therein, a stream of water and dissolved gas passing from the chamber to the main body of water in the vessel.

20. A method as claimed in claim 18 wherein the stream is introduced into the vessel through a jet which is moved to direct the stream at the walls of the vessel to help scour sludge from such walls.

21. A method of breaking down deposits on the walls of a vessel containing a potentially explosive gas mixture, substantially as hereinbefore described with reference to the accompanying drawing.

22. Apparatus for breaking down deposits on the walls of a vessel containing a potentially explosive gas mixture which apparatus comprises means for introducing into the vessel a liquid which is non-combustible and does not support combustion, a source of oxygen-containing gas and means for introducing such gas into the liquid, in use, contained in the vessel so as to enhance the activity of micro-organisms existing, in use, in such liquid, and a source of inert gas and means to supply such inert gas to an ullage space defined, in use, between the surface of liquid in the vessel and the walls of the vessel.

23. Apparatus as claimed in claim 22 wherein the inert gas is a nitrogen-rich gas, separation means being provided to separate an air feedstock into said oxygen-containing gas and said nitrogen-rich gas.

24. Apparatus as claimed in claim 23 wherein said separation means include a bed of adsorbent material which preferentially adsorbs either oxygen or nitrogen.

25. Apparatus as claimed in claim 24 wherein said separation means comprise a pressure swing adsorption system.

26. Apparatus as claimed in claim 24 or claim 25, wherein said separation means comprise a multi-bed adsorbent system and means to operate such system such that the beds operate on similar cycles which are out-of-phase whereby substantially continuous flows of oxygen-containing gas and nitrogen-rich gas are obtained from the system.

27. Apparatus as claimed in any one of claims 22 to 26 wherein said means for introducing an oxygen-containing gas include a diffuser at, or in the vicinity of, the bottom of the vessel through which the gas is introduced in fine bubble form, into liquid, in use, in the vessel.

28. Apparatus as claimed in any of claims 22 to 26 wherein said means for introducing an oxygen-containing gas include means to pass a pressurised stream of liquid into the vessel and means to introduce bubbles of oxygen-containing gas into such stream before it enters the vessel.

29. Apparatus as claimed in claim 28 wherein said means to pass a pressurised stream of liquid include a gas/liquid contactor device in the form of a hollow chamber and means to pass the stream downwardly through such chamber.

30. Apparatus as claimed in claim 29 wherein said chamber has lengths of increasing cross-sectional area in the downward direction to progressively reduce the velocity of the flow through the chamber.

31. Apparatus as claimed in any one of claims 28 to 30 wherein said means to pass a pressurised stream comprise means to withdraw such stream from a body of water in the vessel.

32. Apparatus as claimed in any of claim 28 wherein there is provided in the vessel a jet through which said stream is passed, in use, into the vessel.

33. Apparatus as claimed in claim 32 wherein the jet is mounted such that it can be moved to direct the stream across the walls of the vessel to help scour sludge therefrom.

34. Apparatus as claimed in claim 33 wherein the jet is located within the vessel and is rotatable about a generally vertical axis.

35. Apparatus for breaking down deposits on the walls of a vessel containing a potentially explosive gas mixture, substantially as hereinbefore described with reference to, and as illustrated in, the accompanying drawing.

36. A vessel having apparatus as claimed in any one of claims 22 to 35.

37. A vessel as claimed in claim 36 which is, or is part of, a land based installation.

38. A vessel as claimed in claim 36 which is mounted on a water-borne craft.

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1572800 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

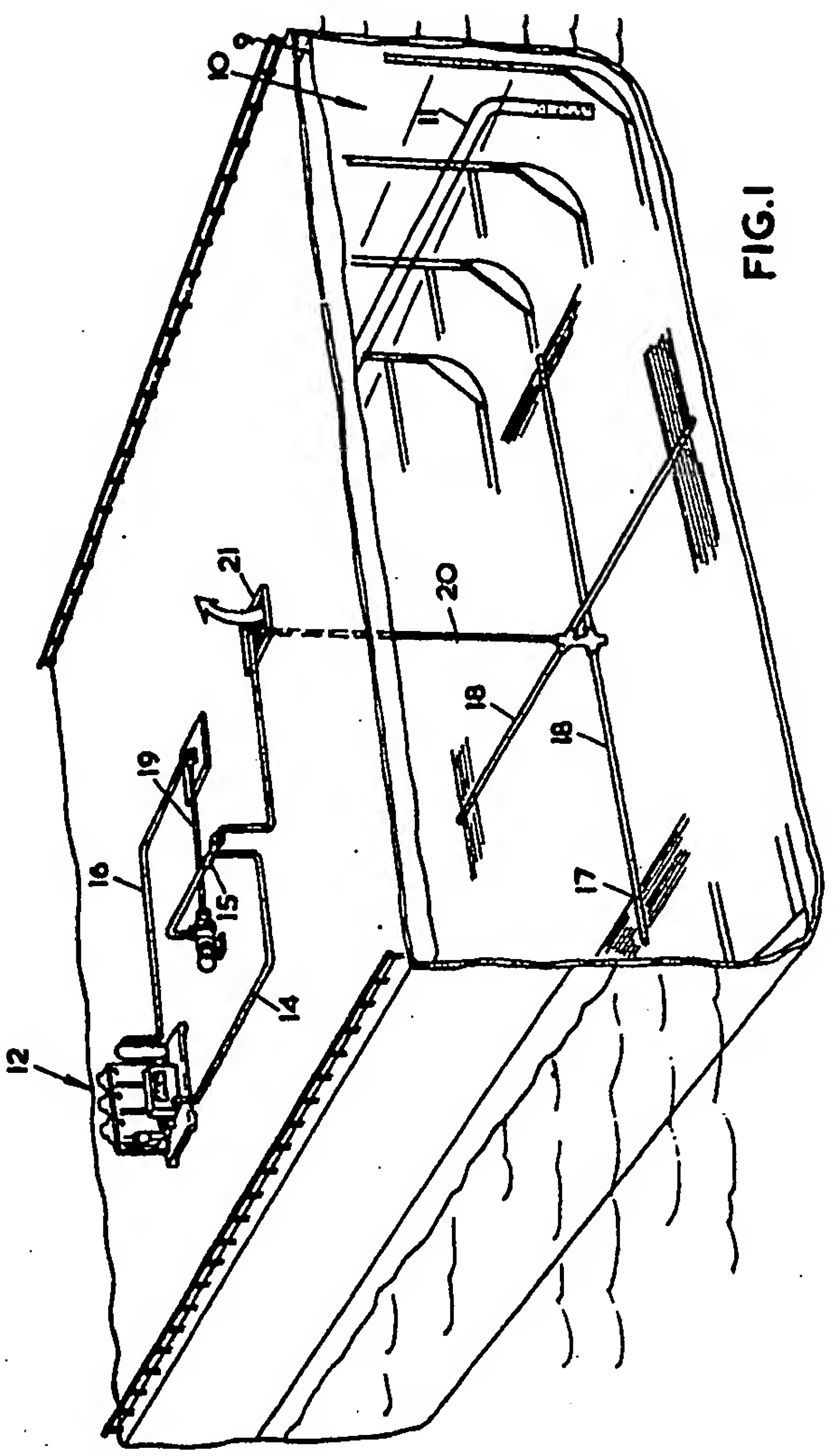

FIG.1

1572800 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 2

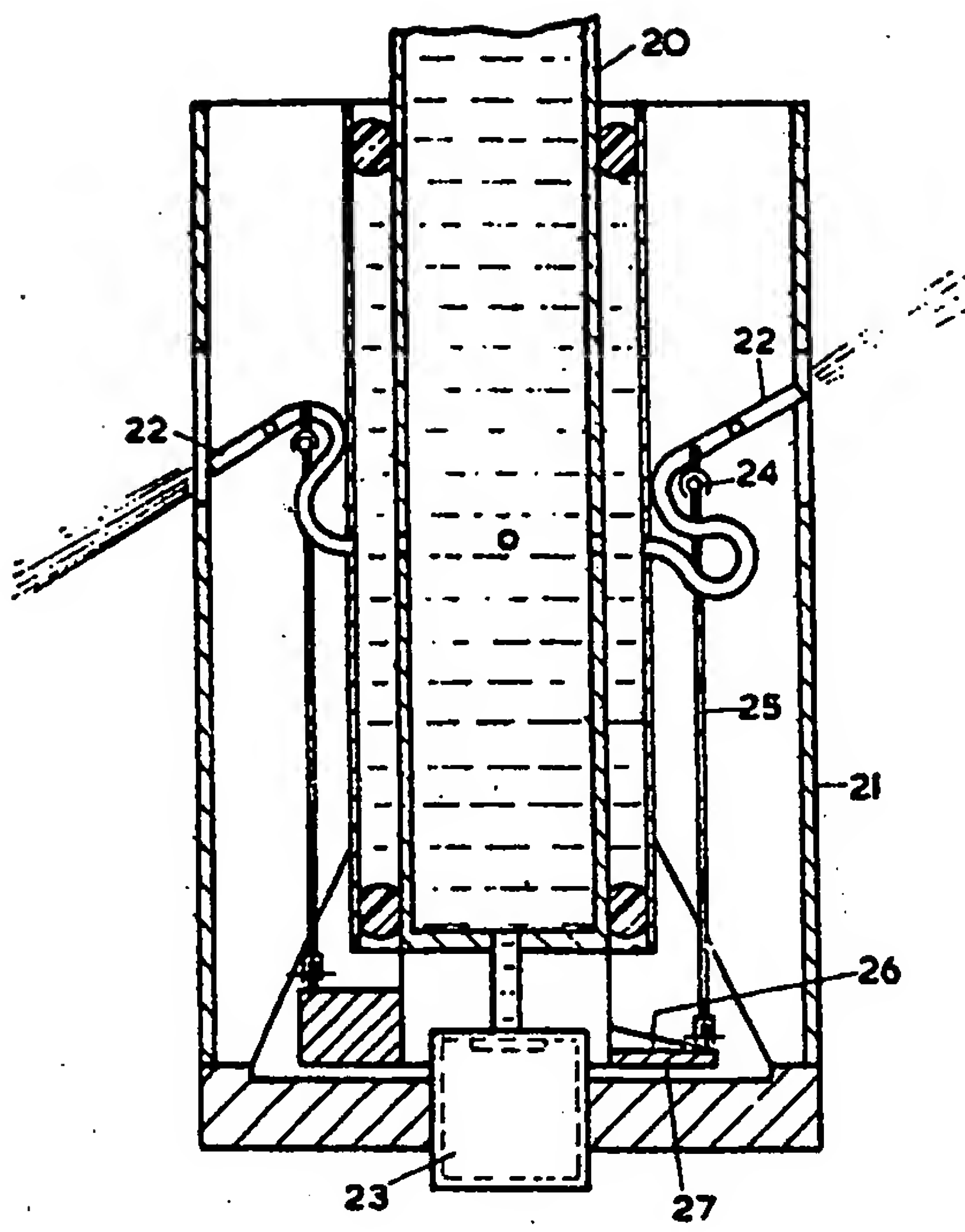

FIG.2